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12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			13. ABSTRACT (Maximum 200 words) The aim is to precisely characterize the tackifier distribution in model pressure sensitive adhesives and correlate variations in this distribution with the adhesives' properties. Work focused on investigating the mechanical properties of the model adhesives near the surface, following the aging of a phase separated model adhesive, and synthesizing and isolating a new model tackifier which is closer in structure to common commercial tackifiers derived from wood rosin. Probing of the surface mechanical properties was done on two scales. Force-distance measurements done with a spherical indenter probed the behavior averaged over lateral areas on the order of millimeters and to depths of order microns. Force-distance measurements done with an atomic force microscope were able to resolve differences in the behavior of various domains in a phase segregated model adhesive and to limit the depth with which the mechanical properties were probed to less than one μ m. In the phase segregated model adhesive a viscoelastic behavior was seen in the tackifier enriched domains, an intermediate behavior in the domain interfaces, and a viscous response in the matrix. The tackifier enriched phase appears to contribute primarily to the surface adhesion. AFM images and force-distance curves were collected for model adhesives of various compositions and after aging for 3.5, 7, 10, and 12 months.		
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TACKIFIER INTERFACIAL SEGREGATION IN PRESSURE SENSITIVE ADHESIVES

FINAL REPORT

Period: Aug. 15, 1995 - December 31, 1999

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A. Paiva, M.D. Foster, E. von Meerwall "Mobility of a Tackifying Resin in a Pressure Sensitive Adhesive" *Journal of Polymer Science. Part B: Polymer Physics* **36**, 373-381, 1998.

A. Paiva, N. Sheller, M.D. Foster, A.J. Crosby, K.R. Shull, "Study of the Surface Adhesion of Pressure Sensitive Adhesives by Atomic Force Microscopy and Spherical Indenter Tests," accepted in *Macromolecules*.

A. Paiva, M.D. Foster, "Aging of Model Pressure Sensitive Adhesives with Scanning Probe Microscopy," *J. Adhesion*, submitted.

Paiva, A.; Sheller, N.; Foster, M. D., "Studying the Surface Adhesion of Pressure Sensitive Adhesives by Atomic Force Microscopy", Proceedings of the 22nd Annual Meeting of The Adhesion Society. Panama City Beach, FL. 1999, p. 412.

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INVENTIONS

none

SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS

First efforts focused on studying the variation in concentration profiles near film surfaces with changes in various system parameters. The most work was done on a model adhesive consisting of polyisoprene (PI) and n-butyl ester of abietic acid (nBEAA), which appears to be a miscible system at room temperature for nearly all compositions.

Changes with tackifier loading

When tackifier loading was varied in the PI/nBEAA system, the neutron reflectivity from the films changed only subtly, suggesting that while quantitative changes occurred in film structure, there were no qualitative changes. The reflectivity data for four different loadings appear in Figure 1. A "bump" near a scattering vector value of 0.087\AA^{-1} appears in all cases, but is always subtle. It is perhaps strongest for the case of 25% tackifier. The variation in adhesive performance with tackifier loading is presented in Figure 2. From these data it is clear that this model system, while well defined, offers very modest adhesion performance and this performance is essentially unchanged with changes in tackifier loading. As an example of the interfacial concentration profiles in these films we consider the particular case of 15wt% loading.

Tackifier composition profile

There are two types of concentration profiles which could yield neutron reflectivity curves consistent with the experimental data. The first type of profile, pictured in Figure 3, envisions interfacial regions enriched with tackifier at both the air surface and substrate surface. This model was also consistent with forward recoil spectroscopy (FRES) results. The fit of the reflectivity data with such a model is shown in Figure 4. The model parameters are summarized in the Table I below.¹

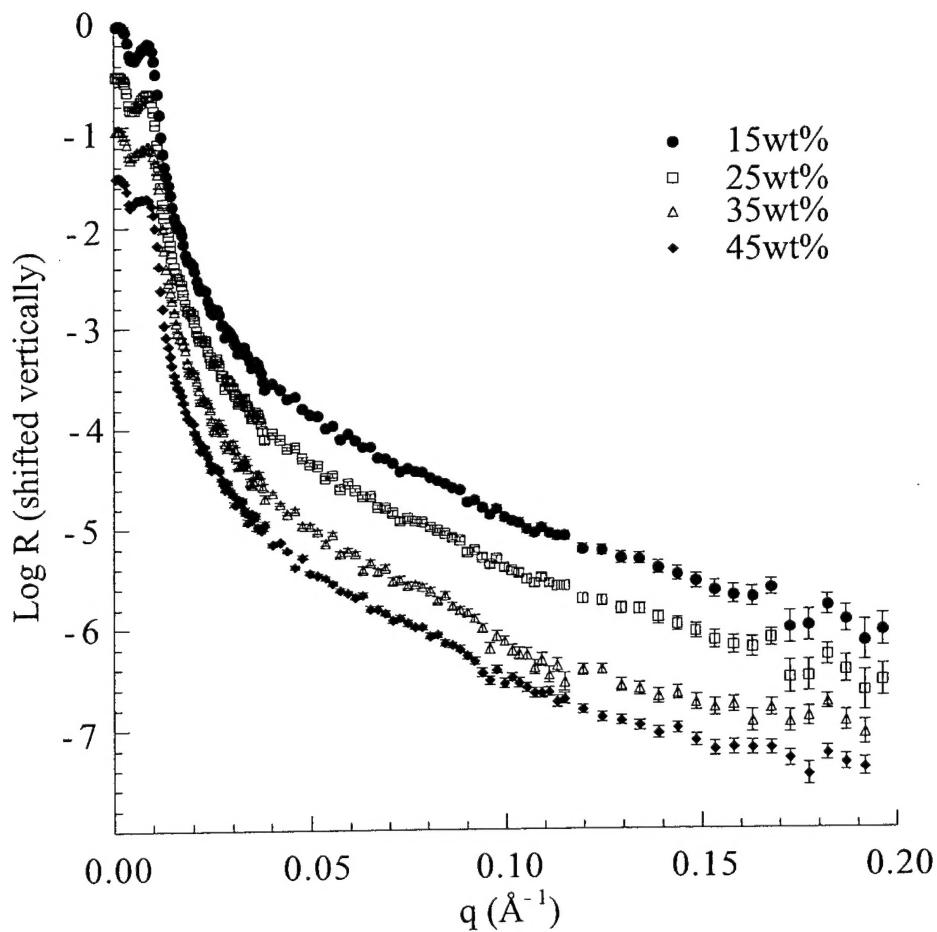


Figure 1 Neutron reflectivity data from samples of PI with four different levels of tackifier show similar features. All indicate nonuniformities in the tackifier concentration.

Footnote:

1. The uncertainty estimates and cross correlation parameters are calculated using a linearized approximation of the behavior of the nonlinear parameter estimation. Strong correlations (cross correlation parameters exceeding 0.65) exist for the following pairs of parameters: b/v of the two enriched layers and thicknesses of the enriched layers.

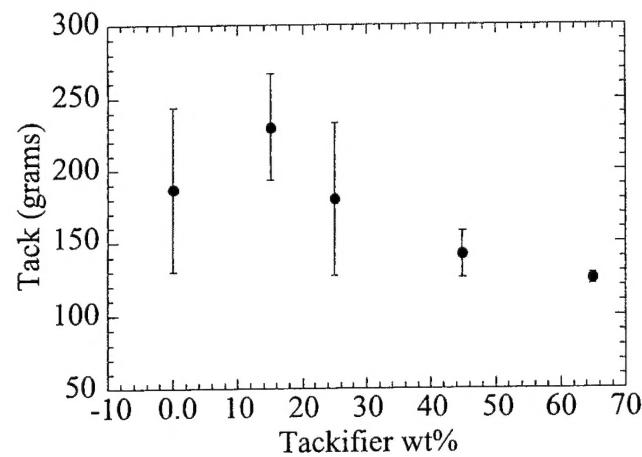


Figure 2. Probe tack as a function of tackifier loading for the PI/tackifier system.

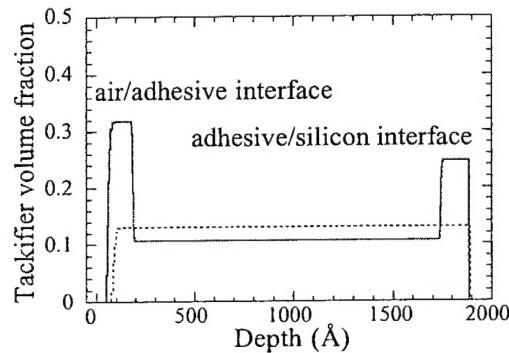


Figure 3. Tackifier concentration depth profile model consistent with the NR data for the adhesive with 15 wt% tackifier. Segregation is seen at both interfaces.

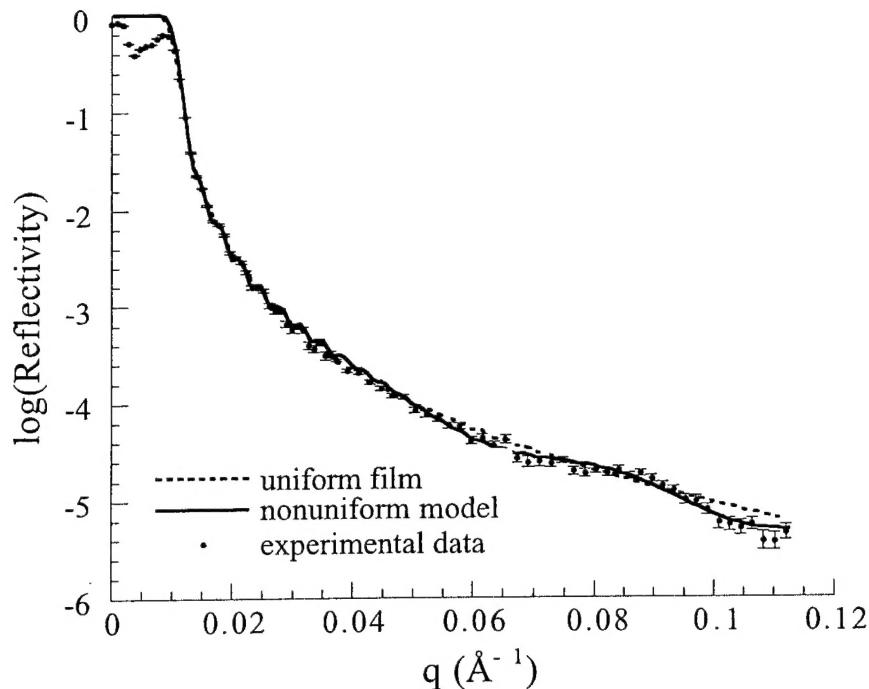


Figure 4. NR data (dots) from the sample with 15 wt% tackifier compared with the reflectivity (solid curve) expected from the model composition profile shown in Figure 3.

Table I.
Parameters of Concentration Profile Model Which Best Corresponds to
Neutron Reflectivity Data

overall thickness	$1837 \pm 4 \text{ \AA}$
air/film roughness, rms	$34 \pm 4 \text{ \AA}$
film/substrate roughness, rms	$4 \pm 1 \text{ \AA}$
thickness of enriched layers	
at surface	$131 \pm 1.4 \text{ \AA}$
at substrate	$149 \pm 1 \text{ \AA}$
compositions (volume fraction)	
surface layer	31.8 ± 6
bulk	10.3 ± 2
bottom layer	24.7 ± 6
interface widths, σ	
top enriched layer/bulk	$\leq 10 \text{ \AA}$
bottom enriched layer/bulk	$\leq 10 \text{ \AA}$

This model has two remarkable features. The first is the abruptness of the transition in concentration from the enriched regions to the "bulk" of the film. The forms of the concentration profiles at these interfaces are modeled with error functions and the error function parameters, σ , must be kept no larger than 10 \AA in order to capture the shape of the reflectivity curve. Such a sharp interface is unknown in the study of polymer/polymer segregation. However, one of the components in the present case has a very small size. While the radius of gyration of the PI chain is about 180 \AA , the radius of gyration for the tackifier molecule it is of order 8 \AA . Apparently this smaller size dominates in determining the characteristic interface width.

The second remarkable feature is the presence of a region of nearly constant composition over more than 100 \AA in depth from the interfaces. No mean field theory presently available could predict such a thick enriched layer. Rather, an exponentially decaying profile would be expected. A small "shoulder" in polymer/polymer surface segregation profiles has been observed by other researchers, but nothing so striking as this. Therefore, other characterization means will be used to verify the presence of these enrichment layers.

A second concentration profile model which can successfully fit the NR data is one which envisions enrichment at both interfaces, but with the concentration decaying into the film in a damped oscillatory fashion. Damped oscillatory profiles have been observed experimentally for thin films of block copolymers and for phase segregating thin films in which the phase decomposition is driven by the surface to create plane waves emanating from the surface. However, two observations argue against the possibility that such an oscillatory profile is present here. First, in contrast to the block copolymer system, there is no connectivity in this system which would tend to drive the formation of an oscillatory profile. Secondly, we have not observed any obvious time dependence to the character of the NR data which would correspond to the temporal development of a spinodal wave. Therefore, although we have suggested the presence of an oscillatory profile in preliminary reports of our work, we do not believe at this time that such profiles are supported by the entirety of the data. Further characterization of the surface layers with other techniques, notably XPS, should help resolve this issue.

Variation with thickness, substrate, and matrix molecular weight

Three variables were altered in order to consider their impact on the observed structure. First, a sample on an etched wafer, rather than an unetched wafer, was measured. That NR data shows the same structure, suggesting a similar film structure. A much thinner film was also considered to check the effect of film thickness. Film thickness also appeared to have only a minor influence on the reflectometry result. Finally, a film with a matrix polymer of molecular weight of 30,000 g/mole, rather than 300,000 g/mole was considered. The NR data from that sample had the same character as well. Thus, our preliminary analysis is that these other variables do not affect the concentration profiles of this adhesive system in strong ways.

Changes with chemistry of matrix or tackifier

Adhesive tack was improved by substituting the tackifier with its hydrogenated analog. Substituting the polyisoprene matrix by its hydrogenated analog, poly(ethylenepropylene) resulted in even larger changes in adhesive tack. In both cases these changes in adhesize performance were accompanied by changes in film concentration profiles. In the case of hydrogenated tackifier, dynamic mechanical thermal analysis (DMTA) indicated the system was still miscible at room temperature. X-ray reflectivity results suggested that the tackifier was no longer enriched at the air surface. When the matrix was PEP, rather than PI, the mixture became immiscible and the polymer enriched the surface. Further study is needed to precisely define the relationship between these observed film structure changes and the corresponding changes in adhesion performance.

1996

Significant progress was made during the 1996 calender year. Efforts focused on three issues: XPS measurements of surface segregation, clarification of bulk miscibility, and characterization of tackifier mobility. The most work was done on a model adhesive consisting of polyisoprene (PI) ($M_w=195,000$ $M_w/M_n\sim 1.05$) and n-butyl ester of abietic acid (nBEAA), which is miscible at room temperature for all compositions. A partially miscible system, containing the hydrogenated analog of polyisoprene, poly(ethylene propylene) (PEP) ($M_w=40,000$ $M_w/M_n\sim 2.30$) and the same tackifier, was also studied.

XPS Study of Surface Concentration

XPS measurements using a cold stage provide, at last, direct evidence corroborating results from neutron reflectivity which indicate that the n-BEAA tackifier segregates to the surface of PI/n-BEAA mixtures in a thin layer. While the XPS can not provide detailed depth profiling information, measurements made at two take-off angles, 20° and 45° , give evidence that the tackifier composition is highest close to the surface. While precise sampling depths for the two take-off angles are difficult to assign, we estimate that the 20° take-off angle probes a nominal depth of $30\text{-}40\text{\AA}$, while the 45° take-off angle probes a nominal depth of $70\text{-}80\text{\AA}$. Examples of survey measurements taken at the two different take off angles are shown in Figure 1. Oxygen, which is characteristic of the tackifier, is clearly more prevalent closer to the surface (at 20° take-off). Measurements were also performed on control samples containing only polymer to assure that the oxygen signal came overwhelmingly from tackifier and not from adventitious species on the surface. Approximate compositions of tackifier inferred from high resolution scans at each take-off angle for four different bulk compositions are summarized in Figure 2. Apparent tackifier weight fractions greater than unity for the bulk composition of 0.25 are evidence that the absolute values of composition are not precise. However, the trends are clear. Compositions inferred from measurements at 20° take-off are always higher than those for 45° take-off, and both are always higher than the bulk composition.

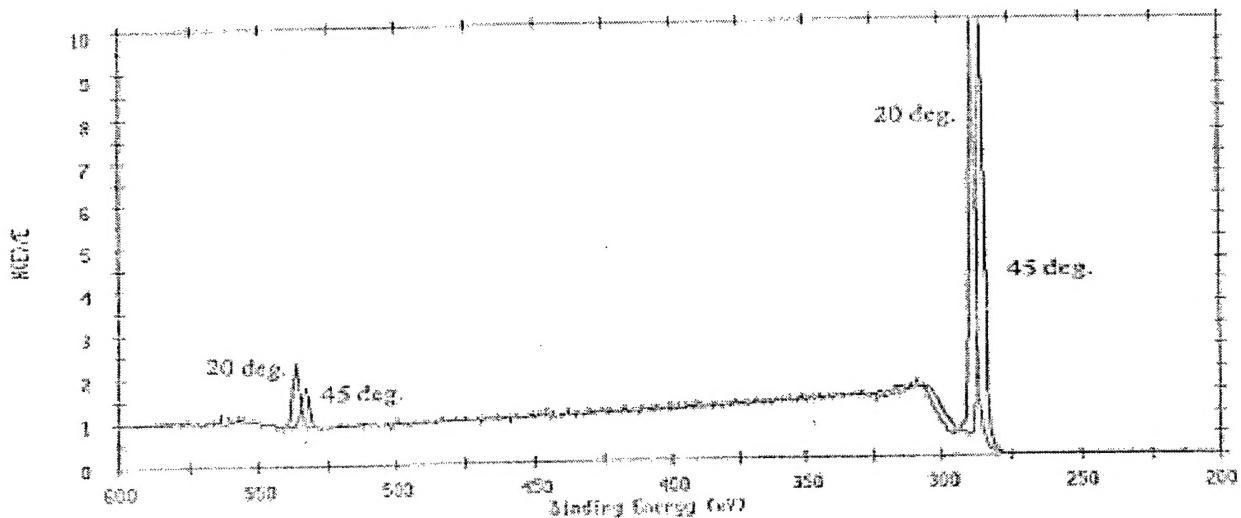


Figure 1. Survey XPS spectra for a sample film containing PI and 15wt% tackifier allowed to equilibrate at room temperature. The peaks on the right are for C1s electrons and those on the left for O1s electrons. The two spectra were measured with a cold stage and take-off angles of 20 and 45 degrees, as indicated. (Discrepancies in peak positions due to different charging are evident, but peak areas alone are critical here.)

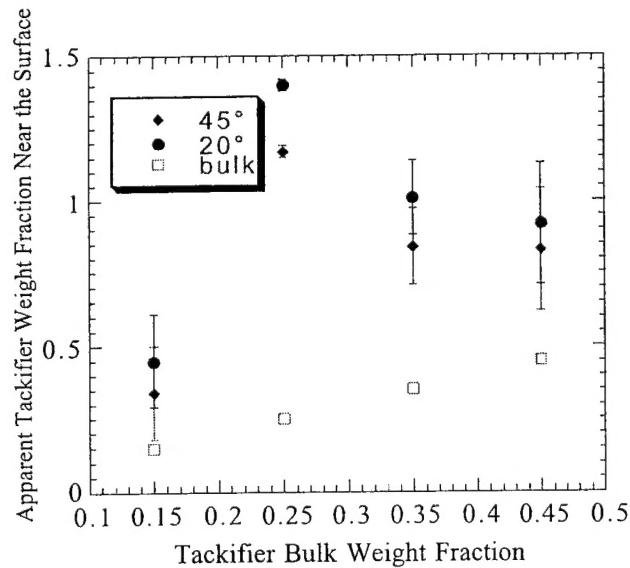


Figure 2. Comparison of tackifier near surface concentrations from XPS data with sample bulk concentrations.

Study of tackifier miscibility

The PI/n-BEAA system is miscible at all compositions at room temperature, but the PEP/n-BEAA systems exhibits a two phase morphology at room temperature for tackifier loadings between 15 wt% and about 95 wt%. Therefore, the phase behavior was studied some with polarized optical microscopy to obtain the schematic phase diagram shown in Figure 3. Since the polymer and tackifier have very different molecular weights the phase diagram is strongly skewed to the right. At 15 wt% the cloud point already lies above 200°C and at 10 wt% it is below room temperature. Figures 4 to 6 show the morphology of blends of PEP/n-BEAA with 15, 35 and 50 wt. % tackifier at 40°C, respectively.

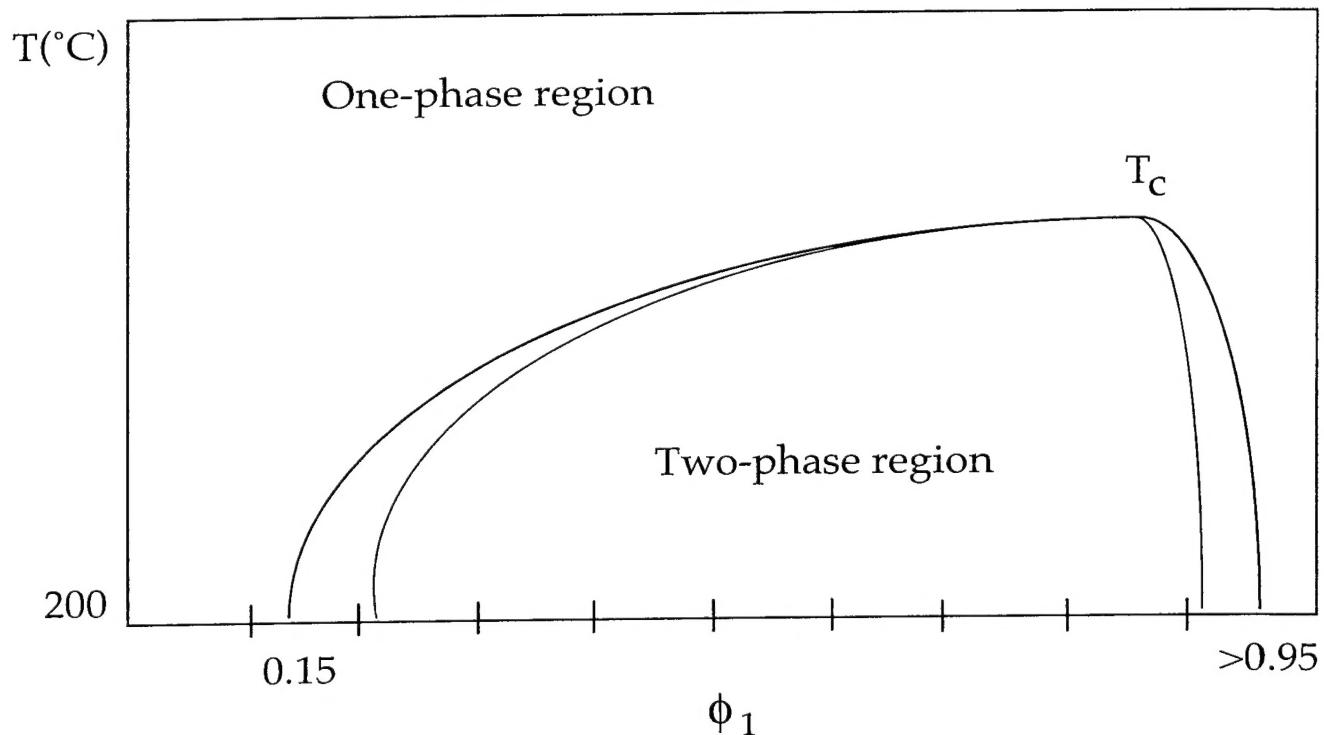


Figure 3. Approximate phase diagram for blends of PEP/n-BEAA. The thick curve represents the binodal and the thin curve the spinodal. T_c appears at a composition close to $\phi_1=1$.

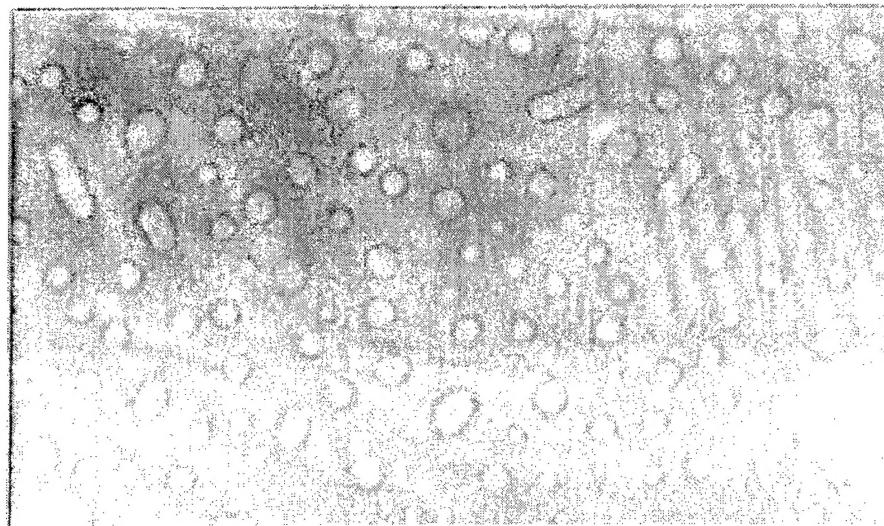


Figure 4. Morphology of blend of PEP/15 wt.% n-BEAA at 40°C.

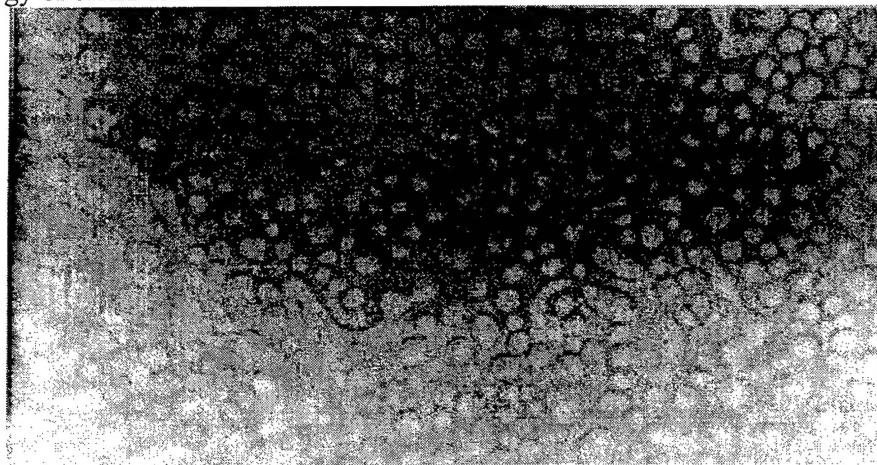


Figure 5. Morphology of blends of PEP/35 wt.% n-BEAA at 40°C.

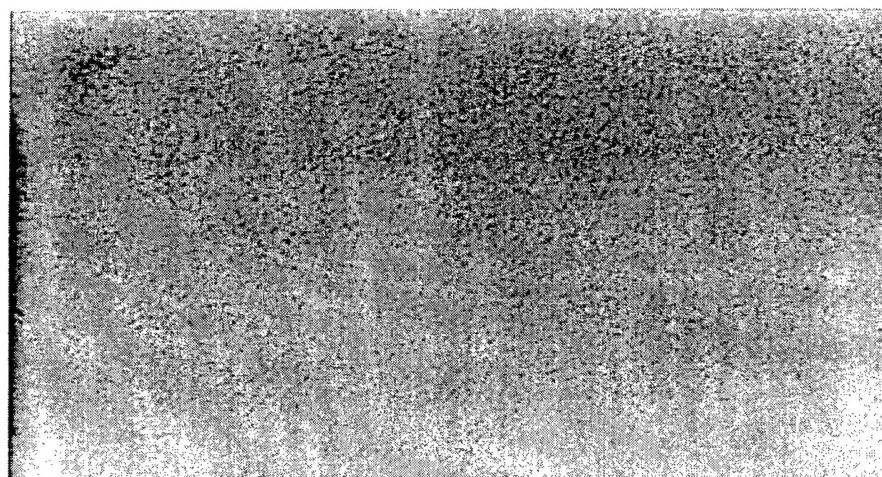


Figure 6. Morphology of blends of PEP/50 wt.% n-BEAA at 40°C.

Study of tackifier mobility

Diffusion measurements were performed using a Spin-Lock, Ltd., Model CPS-2 33-MHz NMR spectrometer attached to a microcomputer. Details of the equipment have been presented in several papers by von Meerwall *et al.*^{1,2}. The diffusion coefficients were determined at 30°C, 40°C, 50°C and 70°C. Data for the PI/n-BEAA system are shown in Figure 7.

Abietic ester of rosin acid in polyisoprene

The self diffusion coefficient of the tackifier in the adhesive increases gradually and only slightly as the tackifier loading increases. This seems consistent with the fact that the tack varies only modestly with tackifier loading in this system. The temperature dependence could be fit well using a WLF-type expression and the concentration dependence modeled using the free volume theory of Vrentas-Duda. The solid line in Figure 7 represents the fit to the Vrentas Duda theory. The free volume of the tackifier was found to be nearly identical to that of the polymer, with the slight upward trend in the diffusion coefficient coming about solely as a result of the difference in polymer and tackifier densities. Thus this molecule which tackifies only subtly neither plasticizes nor antiplasticizes.

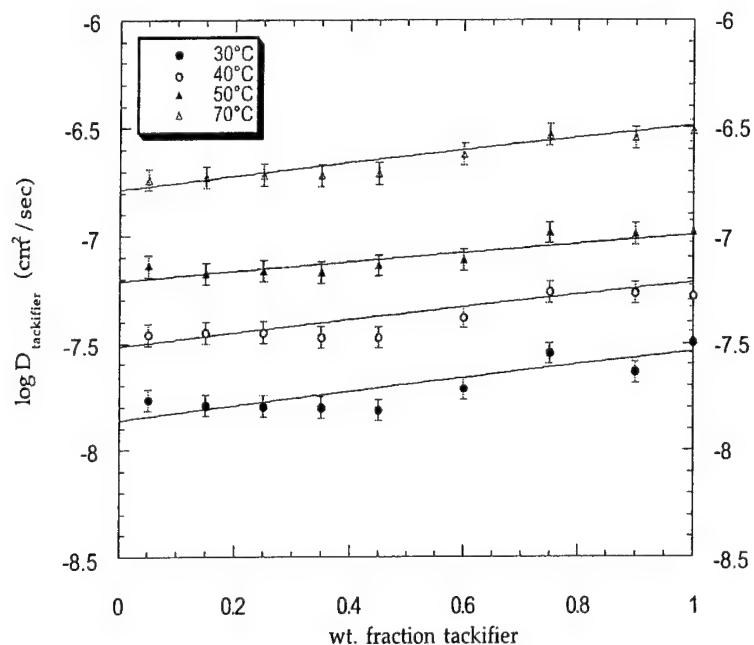


Figure 7. Concentration dependence of the tackifier's diffusion coefficient in polyisoprene at different temperatures. Solid line represents fit to the Vrentas Duda theory. $M_1/M_2 = 1.0$

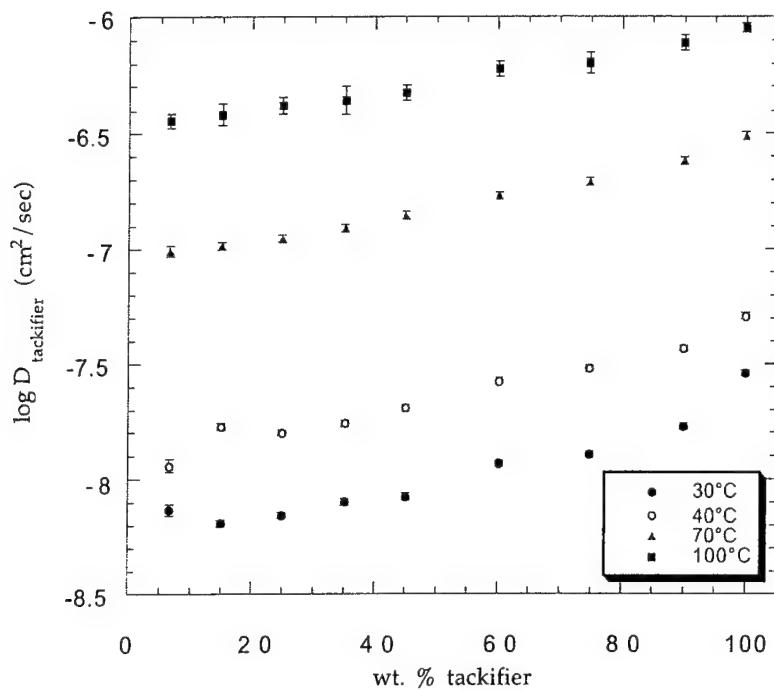


Figure 8. Self diffusion coefficient of the tackifier as a function of wt. % of tackifier in PEP/tackifier samples. Measurements taken at four different temperatures.

Abietic ester of rosin acid in poly(ethylene-propylene)

The tackifier's self diffusion coefficient in mixtures with PEP increases gradually and slightly as the amount of tackifier increases, as shown in Figure 8. The tackifier mobility is always higher in PI than in PEP, despite the fact that the molecular weight of the PEP matrix is lower. It is not possible to attempt to explain the results with the free volume theories available for miscible systems, due to the two phase morphology present here. However, the behavior seen is quite intriguing. A schematic of what was expected is shown in Figure 9. It had been anticipated that for tackifier loadings corresponding to a two phase morphology two diffusion coefficients would be observed, one characteristic of the polymer rich phase and one characteristic of the tackifier rich phase. The resolution of the measurements was sufficient that two such coefficients would have been observable, even though there wasn't a large difference between the tracer coefficient of tackifier in polymer and the coefficient of tackifier in neat tackifier. It is also notable that the tack of the PEP/n-BEAA adhesive varies strongly with composition, reaching a maximum at about 35 wt% tackifier, even though the self diffusion changes little. Further work is needed to address the issue of how the mutual diffusion coefficient changes in this case. The mutual diffusion coefficient actually determines the rate at which tackifier may be redistributed in the adhesive, and it depends not only on the inherent mobility of the tackifier, but also on the thermodynamics of the system.

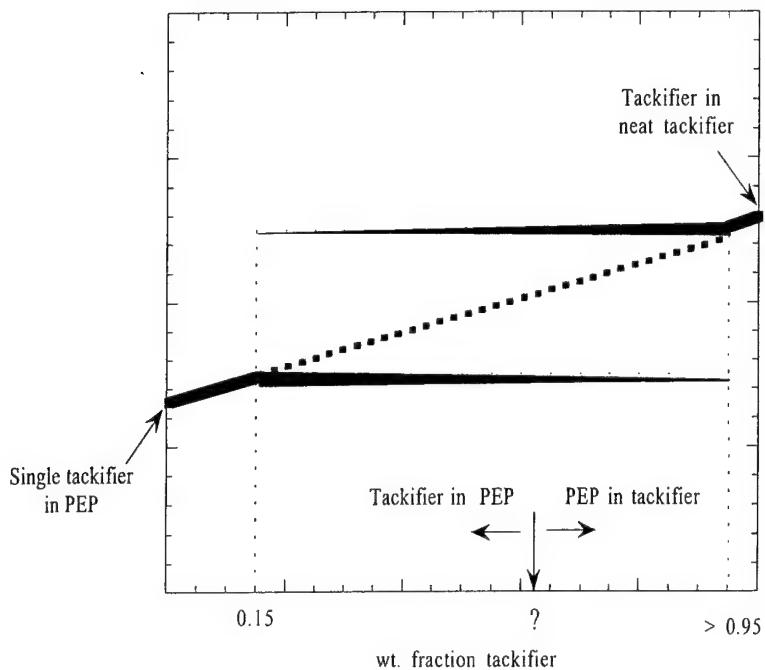


Figure 9. Schematic representation of how the tackifier's diffusion coefficient was expected to change with weight fraction of tackifier in the blends which display two phases for intermediate compositions.

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2. von Meerwall, E. D.; Ferguson, R. D. *J. Appl. Polym. Sci.* **1979**, *23*, 3657.
3. Li, X. Ph. D. Thesis, The University of Akron, 1996.

1997

Significant progress was made during 1997. Work dealt with three issues. First another type of model tackifier, hydrogenated polystyrene (PVCH) was investigated. Secondly, measurements of tackifier mobility were made on two model systems which closely approximate a commercial adhesive. They contain only elastomer and tackifier, but the tackifiers are commercial products, Pentalyn A and Pentalyn H, both of which are chemically similar to the model tackifier, n-butyl ester of abietic acid (n-BEAA) used in much of the rest of the work. The third focus of the work was probe tack measurements done using a spherical indenter (referred to as "JKR experiments" in last year's report). This technique allows one to gather more detailed information about the adhesive behavior than is possible with the simple commercial probe tack test.

Model tackifier PVCH

The PVCH was made by hydrogenation of polystyrene of a molecular weight which is low for polymers, but much higher than the MW of the n-BEAA model tackifier. PVCH has been used as a tackifier in studies¹⁻³ by other authors. Using the higher molecular weight tackifier should make certain measurements requiring vacuum environments (SIMS, XPS, FRES) much easier. Obtaining the required hydrogenation took much longer than planned and then the material of molecular weight 2000 provided to be immiscible with PI. The immiscible blends were not at all tacky, but rather brittle. Measured tack values were essentially zero. A lower molecular weight PVCH is needed. Due to the difficulty of obtaining hydrogenation of these materials, work on this type of tackifier has been suspended for the present.

Mobility of commercial tackifiers

The mobilities of two commercial tackifiers in model matrices were studied by PGSE-NMR. Pentalyn A, a hard, thermoplastic resin, has as its primary component the pentaerythritol ester of refined rosin. Of course, as with all commercial tackifiers, there are many other secondary components which are not readily characterized. Pentalyn H is also predominantly composed of pentaerythritol ester of a rosin, but it has been stabilized by hydrogenation to improve resistance to oxidation and thermal degradation. The pentaerythritol ester is much larger than the n-BEAA molecule used widely in our current work.

PGSE-NMR experiments for the neat tackifier were performed at 150.5°C, fitting the data to a model where a small spread in diffusion coefficients is taken into account. The average diffusion coefficient obtained was $3.4 \times 10^{-8} \text{ cm}^2/\text{sec}$ for Pentalyn A and $3.5 \times 10^{-8} \text{ cm}^2/\text{sec}$ for Pentalyn H. The results indicate that while Pentalyn A has a spread of diffusion coefficients of 1.12, Pentalyn H has a spread of only 0.022. These results make Pentalyn H a good tackifier to study by PGSE-NMR, since Pentalyn H is widely used and high values of tack are expected as well as a concentration dependence of tack with composition. In this way it will be possible to answer the question of whether or not mobility of the tackifier affects the tack adhesion.

Blends of both commercial tackifiers were made with polyisoprene (number average molecular weight of 195,000 and a molecular weight distribution less than 1.1). The compositions chosen were 5, 30, 70 and 90 wt %. The selection was made based on results of other researchers which show a maximum tack obtained at a composition of 70 wt. % of Pentalyn H in natural rubber. In those studies a two phase morphology was observed in compositions from 40 up to 85 wt. % of Pentalyn H.

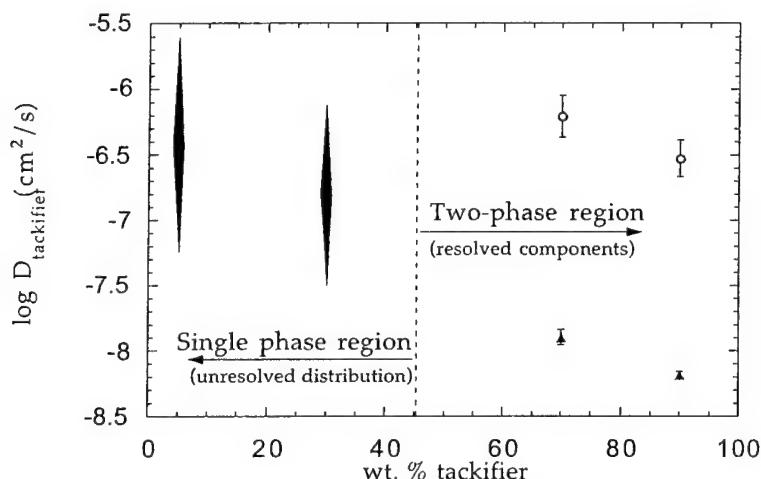


Figure 1. Diffusion coefficient of Pentalyn H as a function of wt. percent tackifier in PI/Pentalyn H samples. For compositions known to exhibit a single phase, a broad range of tackifier mobility is seen. In the region of composition where two phases have been observed two different tackifier mobilities may be readily resolved.

PGSE-NMR experiments were done at 50.5°C and 100.5°C. The results for the lower temperature indicated that only the samples with 5 and 30 wt. % of Pentalyn H and 5 wt. % Pentalyn A showed an echo at 25 msec. This indicated that the spin-spin relaxation times (T_2) of the highest concentration samples were very short. Thus it was not possible to see the diffusion of the tackifier at this instrument setting. At 100.5°C the mobilities could be studied. In the region of compositions for which the PI/Pentalyn H blend is known to be

miscible, the measurements indicate a broad range of mobilities, while for compositions for which the system has two phases two reasonable distinct mobilities are resolved as shown in Figure 1. Similar results were found for Pentalyn A. These results provide an interesting contrast to those for the PEP/n-BEAA system reported last year in which no manifestation of the two phase structure was found in the diffusion measurements.

Probe tack measurements

Probe tack measurements have been carried out in collaboration with Prof. Ken Shull at Northwestern University using a spherical indenter setup intended for Johnson, Kendall, and Roberts (JKR) adhesion tests. Analysis based on the JKR theory⁷ of contact mechanics may be used for elastic solids and recently corrections have been proposed for use with viscoelastic solids. For the viscous (uncrosslinked) adhesives considered here the JKR analysis is no longer valid, but the apparatus can nonetheless be used to yield important information on the adhesion behavior. The great advantage of the technique, as opposed to measurements with the conventional probe tack device, is that force-distance information is collected for the entire bonding and debonding process. It also offers some advantages over peel tests and probe tack experiments because in those techniques the measured energy release rate (G), or the energy required to extend an interfacial crack by a unit area, is dominated by bulk viscoelastic energy losses due to deformations of the sample⁶⁻⁸. The spherical indentation experiment is performed at very low rates of crack velocities, thus interfacial effects are not masked by bulk effects. Also, the sample volume is very small, which allows smooth and well-defined contact as well as a considerable reduction in bulk dissipation losses^{9,11}.

The contact area, a , is monitored by optical microscopy as a function of the applied load. The load can be varied during the experiment by displacing the microscope stage vertically using a stepper motor⁹. Figure 2 shows a schematic result obtained for loading and unloading experiments.

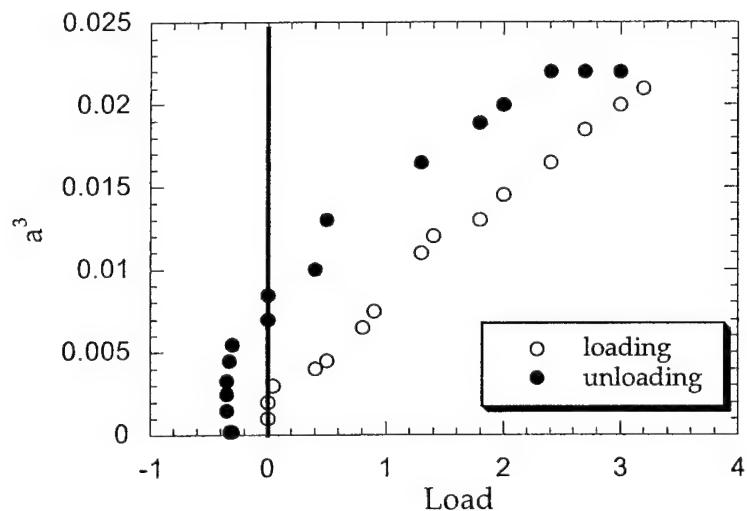


Figure 2. Loading-unloading curve of a JKR experiment

Experiments were performed on pressure sensitive adhesives made from polyisoprene with two different tackifiers: a model tackifier n-butyl ester of abietic acid (n-BEAA) and a commercial tackifier (Pentalyn-H). The purpose of studying two tackifiers was to compare the adhesion hysteresis of a tackifier that has been widely used commercially and has good tackifying action with that of model tackifier which provides moderate performance. A third, polyethylene-propylene (PEP) with the model tackifier, was also studied. This system shows no surface segregation of tackifier and higher values of conventional adhesive tack when compared to the PI/n-BEAA system. The three systems also differ importantly in that the PI/n-BEAA mixture is miscible at all compositions, while the

PI/Pentalyn H mixture shows two phases from 40 to 85 wt% tackifier⁶. The PEP/n-BEAA system also shows two phases for compositions from 15 to 95 wt% tackifier. Samples were prepared by solution casting using an Accu Gate™ fluid spreader. Film thicknesses ranged between 2 and 3 mils (50 to 75 μm).

The experiments were performed in Professor Shull's laboratory. The details of the equipment have been described recently in the literature⁹. The adhesives were pressed against a glass hemisphere with a radius of 3.175 mm at a displacement rate of 2.5 $\mu\text{m/s}$. When a maximum load of 25 mN was reached the sphere and adhesive were held in contact for one second, after which unloading started at the same rate of displacement.

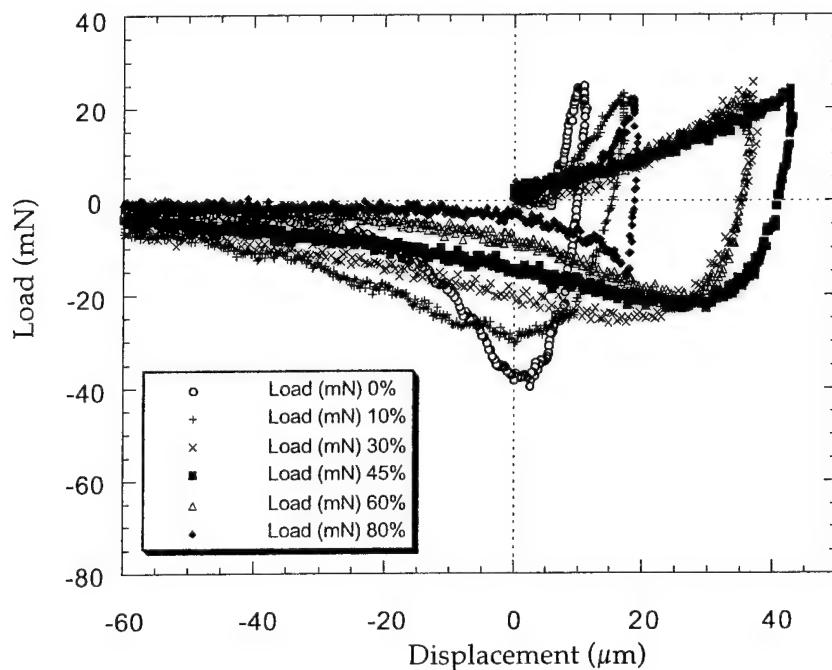


Figure 3. Load-displacement curve for PEP/nBEAA at different tackifier composition. The stiffness of the adhesive changes little with tackifier composition, indicated in the legend.

The load displacement curves for the different adhesives are shown in Figures 3 - 5. All the samples showed fluid-like behavior. Nevertheless, information about the stiffness of the sample can be obtained qualitatively from the slope of the loading portion of the curve. The area under the curve may still be used quantitatively as a measure of the energy required to break the adhesive bond (adhesion energy). For the PEP/nBEAA system the stiffness varies little with tackifier composition, while some changes are observed in the PI systems, those being more pronounced with nBEAA than with Pentalyn H. The PI/nBEAA adhesives are the most soft. Comparing the curves for 45 wt% tackifier for each system, one sees the greatest decrease in stiffness with tackifier composition for PI/nBEAA. In that case the glass hemisphere penetrates a distances of about 40 μm , which is at least a factor two larger than for the other two systems. The behavior of PI with both tackifiers is similar (see Figure 4 and 5). Initially as tackifier is added it acts as a plasticizer. However once a certain composition is passed the adhesive becomes stiffer.

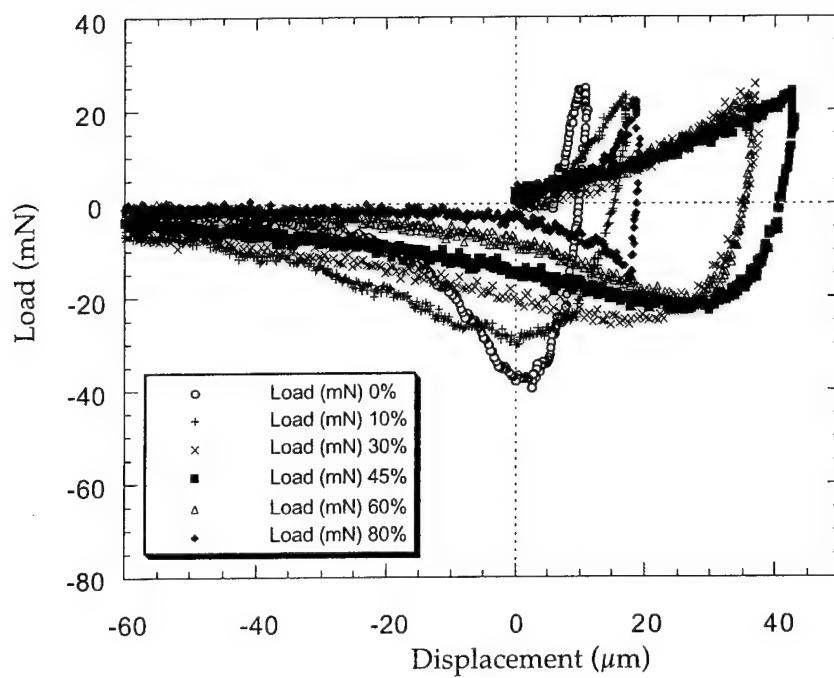


Figure 4. Load-displacement curves for PI/nBEAA at different tackifier compositions.

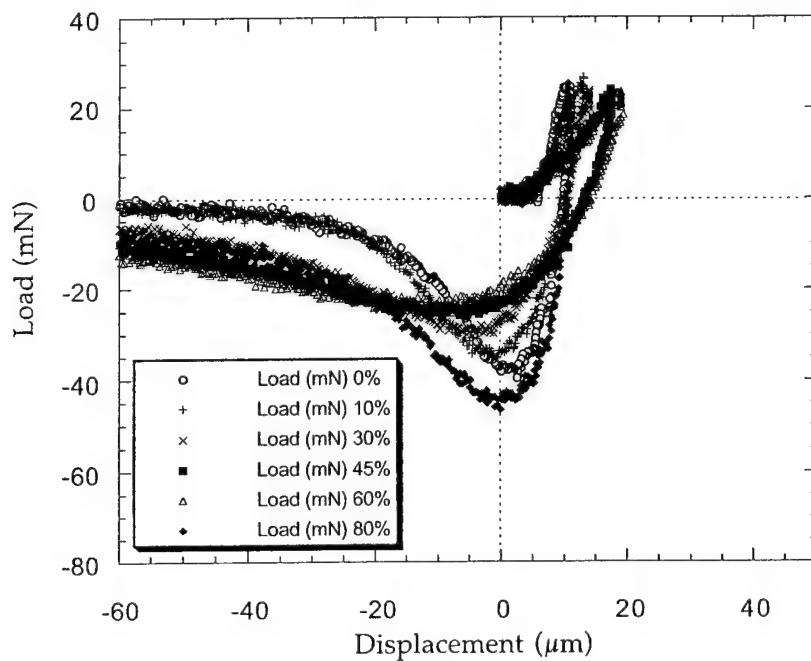


Figure 5. Load-displacement curves for PI/Pentalyn H at different tackifier compositions.

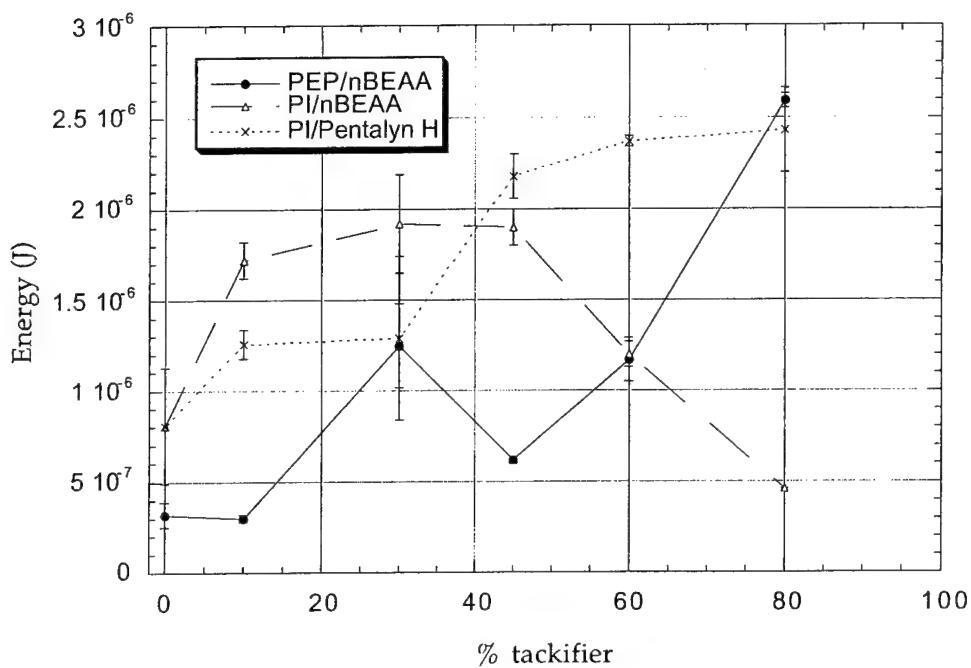


Figure 6. Variation in adhesive energy with tackifier loading for the three systems measured with the spherical indenter.

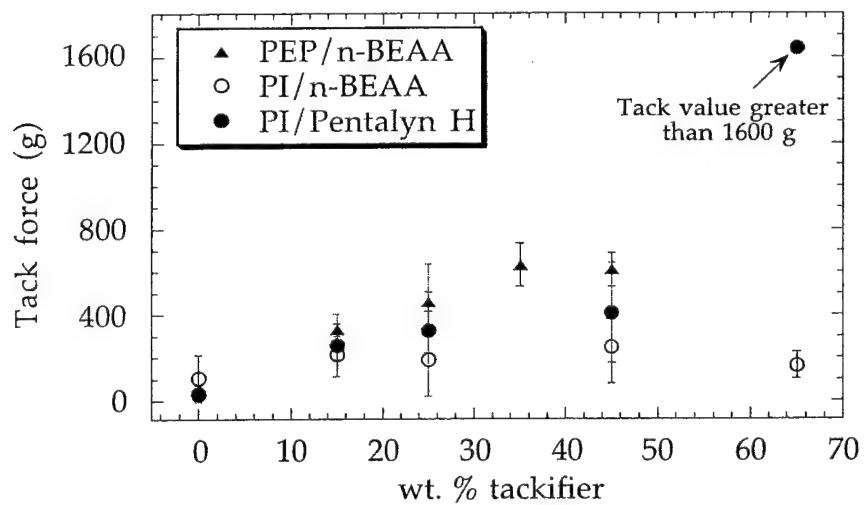


Figure 7. Tack values for blends of PEP/n-BEAA, PI/n-BEAA and PI/Pentalyn H measured with conventional probe tack device (ASTM D 2979-88) as a function of tackifier composition.

Figure 6 shows the variation of adhesive energy with tackifier composition as calculated from the area under the load-displacement curves for all three systems. The error bars are calculated as the standard deviation from three to five measurements performed for each composition. The PI/n-BEAA system shows a clear, broad maximum around 25 wt% tackifier, which differs from the conventional probe tack results, shown in Figure 7,

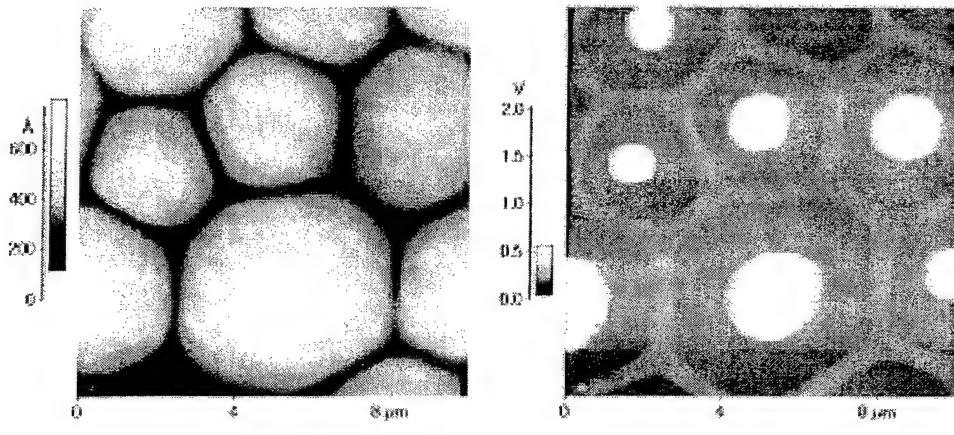
which suggest only weak change in tack with composition. The PEP/n-BEAA system shows an increasing adhesion energy at the highest tackifier composition tested with the spherical indenter method. Conventional probe tack data is not yet available above 45 wt% tackifier for that system. The PI/Pentalyn H system shows an adhesion energy which is increasing still at 80 wt% tackifier for both methods. The displacement rate is very slow here and that must be kept in mind. For these experiments the speed is 2.5 $\mu\text{m/s}$, which is to be compared to 10 mm/s used in conventional probe tack measurements. Fibrillation plays an important role at low rates and it dominates in the spherical indenter experiments, while in the probe tack measurements no fibrillation is observed.

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1998

Good progress was made on three fronts in the work. First the *surface mechanical properties* of model pressure sensitive adhesives (PSAs) have been probed with the tip of an atomic force microscope to provide information on a more local scale than available from the measurements with a spherical indenter. Results of the work with the spherical indenter (done in collaboration with Prof. K. Shull) were presented in last year's report. The approximate contact areas achieved using the AFM probe are ca. μm^2 as compared to mm^2 for the spherical indenter. The forces probed with AFM are on the order of nN, while those probed with the spherical indenter are on the order of mN and the penetration depths are only several hundred nm for AFM, but several μm for the spherical indenter. The comparison of the results from these two different types of measurements provides a preliminary suggestion as to which phase dominates the surface adhesive in the commercially important case of a phase segregated adhesive. The second area of progress was in studying *aging* in the morphology of a model adhesive over a 12 month period. Thirdly, a new model tackifier, a diester of abietic acid, was synthesized.



a) Topographic image

b) LFM image

Figure 1. Example of images acquired in contact mode for PEP/80 wt.% n-BEAA. Samples were seven months old. a)Topographic image. Bright areas represent high topographic features. b)Lateral force microscopy image. Bright areas represent high surface friction regions in the sample.

Sample materials and preparation

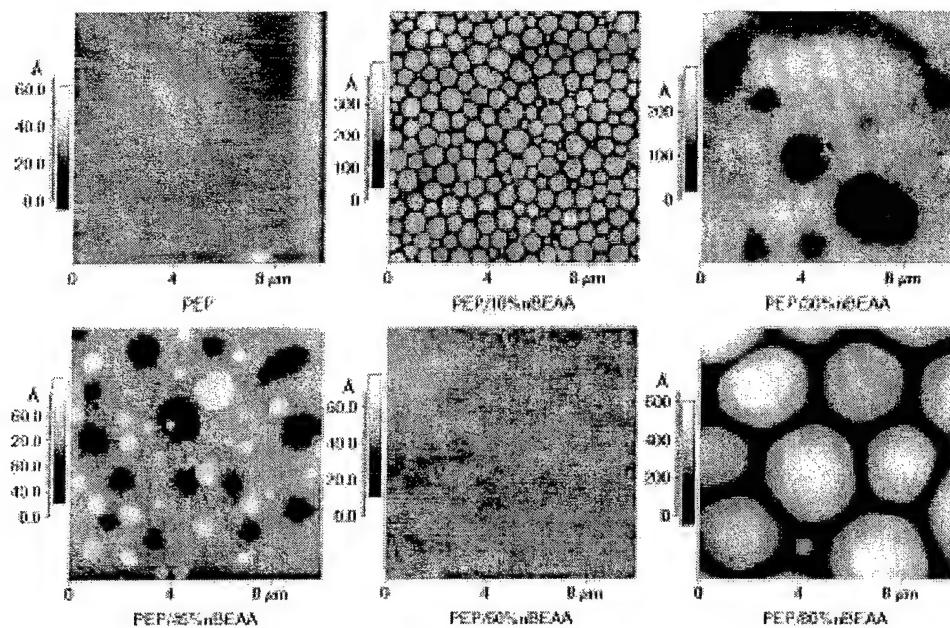
Poly(ethylene propylene) (PEP) with a weight average molecular weight of 244,000 and a polydispersity index of 1.7 was used as the rubber component. It was obtained by the diimide hydrogenation of polyisoprene. The model tackifier used was n-butyl ester of abietic acid (nBEAA). Friction properties and surface topography of blends with compositions from 10 to 80 wt % tackifier were studied with lateral force microscopy and contact mode microscopy, respectively. This adhesive showed a two-phase morphology at room temperature as observed by optical microscopy[1] and AFM topographic measurements. Surface adhesion measurements were performed on a sample of PEP and a blend of 80 wt. % tackifier in PEP. All samples were prepared by solution casting on microscope slides using an Accu Gate™ fluid spreader. Film thickness ranged between two and three mils (50 to 75 μm).

AFM measurements

Atomic Force Microscopy measurements were performed using the Autoprobe™ M5 (Park Scientific Instruments). AFM experiments allowed the determination of the film's adhesive properties as well as the study of the topography of the samples. Topographic and friction images of sample's surfaces were obtained under ambient conditions in contact mode according to established procedures [2-4]. Local adhesive and viscoelastic properties were measured by indenting the surface with the tip at different points along a line and recording cantilever deflection as a function of tip to sample distance (force-distance measurements)[2-4]. Each line was chosen to begin inside a tackifier enriched domain and cross over into the matrix as illustrated in the inset of Figure 4. Measurements were performed at a displacement rate of 2.5 $\mu\text{m/s}$. Silicon probes (Ultralever™, Park Scientific Instruments) with V-shaped cantilevers and conical tips with typical radii of curvature of approximately 10 nm were used for all measurements (as reported by the manufacturer). For a quantitative

study of the adhesion forces, precise values of both the cantilever deflection and spring constant were indispensable[5-7]. The spring constant of the cantilever used in this study was experimentally determined to be 0.41 ± 0.03 N/m following the procedure described by Tortonese *et al.*[7].

Figure 2. Examples of topographic images acquired in contact mode for PEP/n-BEAA at several tackifier



compositions. Samples were seven months old.

Topography and surface friction

An example of a topographic image in contact mode of the blend of PEP/80 wt. % n-BEAA is shown in Figure 1a. At the moment this image was taken, the sample had been cast for 7 months. It can be observed that the domains appear to extend above the matrix, reflecting the fact that the matrix deforms more readily than do the domains. The domains' heights may be accentuated due to two effects, differences in the moduli of the domains and the matrix, and differences in solvent evaporation rate between the two phases. This last effect has been reported by others [8] for polymer/polymer blends. Differences in friction between the domains and matrix can be clearly observed in the LFM image (Figure 1b). The dark areas represent regions of low friction while the bright ones represent regions of high friction. From these images it may be inferred that the domains are tackifier enriched (having the higher friction) while the matrix is polymer enriched. A preferential dissolution of the tackifier enriched phase was performed using acetone and confirmed that the domains were tackifier enriched.

Preliminary results of topographic measurements of blends at other compositions show differences in the structure with composition and time. Figure 2 shows topographic images of PEP/nBEAA blends at several compositions when the samples were 7 months old. An aging of the structure over months was observed for these blends, except for PEP/60wt.% nBEAA, which remained unchanged. Images were acquired at 3.5, 7, 10 and 12 months. Growth of the domains and in some cases coalescence was observed. In Figure 3 the time dependence of the structure PEP/10wt.% nBEAA is shown. A slight increase in the size of the domains as well as coalescence is observed. The structures that appear at 10 and 12 months indicate that the matrix is disappearing and that if enough time elapses the system will be homogenous. Other experiments and the analysis of the force-distance curves are being undertaken to characterize this time and composition dependence.

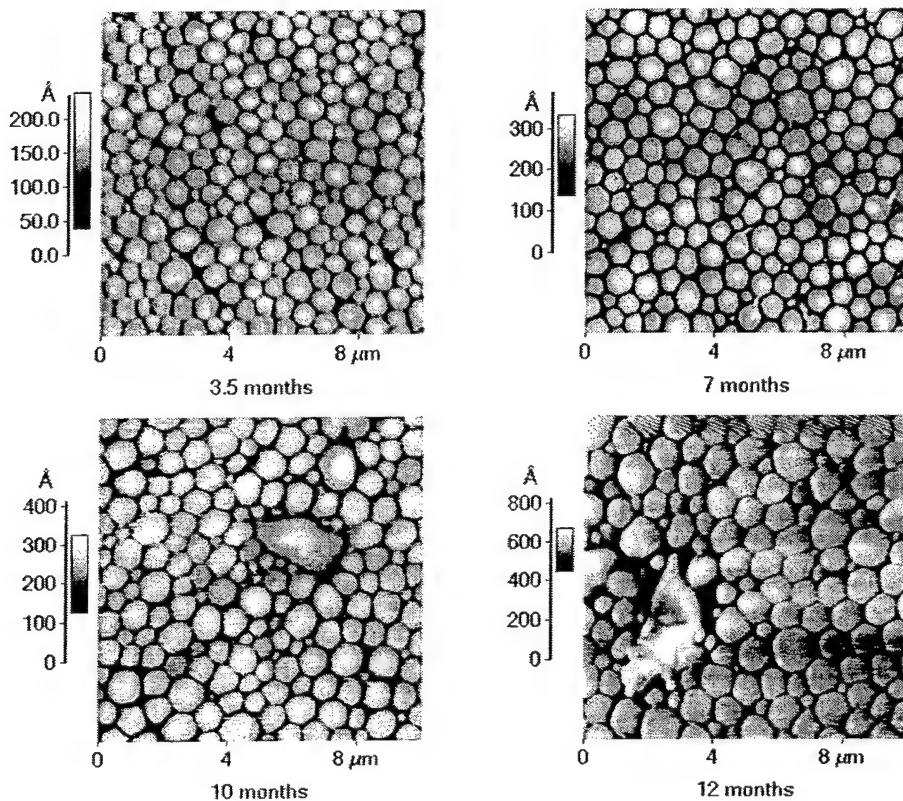


Figure 3. Topographic images of PEP/10wt.% nBEAA showing changes in time for samples aged 3.5, 7, 10, and 12 months. False color scales all correspond to a range of 200Å.

Force - distance curves

The force vs. distance curves obtained by indenting the PEP/80 wt. % n-BEAA blend with an AFM tip are shown in Figure 4. Three different types of behavior are observed, a viscoelastic behavior within the domains, a transition behavior in areas close to the edges of the domains and a more dissipative response in the matrix which is rich in polymer. While the snap-back in the domains is sudden, this is not the case in the matrix where strong bulk deformation is observed.

The area under the curve indicates how much energy is required to break the adhesive bond (adhesion energy). For comparison of these results with adhesion measurements done by other techniques, the integral of the force-distance curve is normalized by the estimated maximum contact area. For PEP the value of energy per unit area is only 2.6mJ/m^2 and a slight increase is observed to 8.6mJ/m^2 in the polymer enriched phase of the blend. The tackifier rich domains show values of 28.7mJ/m^2 . This indicates that the tackifier enriched phase mainly contributes to the surface adhesion in this PSA. Future work will include the study of a system that shows good performance as a PSA, but differs from the one considered here that it is miscible over the whole range of composition. In this case the study of a single phase system will be done to determine how the surface adhesion varies with composition.

Comparison of the results obtained by AFM nanoindentation with those obtained on the same system

with spherical indenter tests[9] indicates that the force per unit area on an AFM tip is three orders of magnitude lower than those obtained using a glass hemispherical indenter six mm in diameter. Penetration depths are only several hundreds nm for AFM, but several μm for the spherical indenter. This large difference in penetration depth could explain the large difference in adhesion energies measured by the two experiments. This would be the case if the vast majority of the energy is dissipated in the bulk and not in the near surface region. Another source of discrepancy in the results could be the uncertainty in the estimation of the contact area with AFM. This could explain perhaps a factor of 10 discrepancy, but the largest difference comes from the fact that penetration depths are very different between the two experiments.

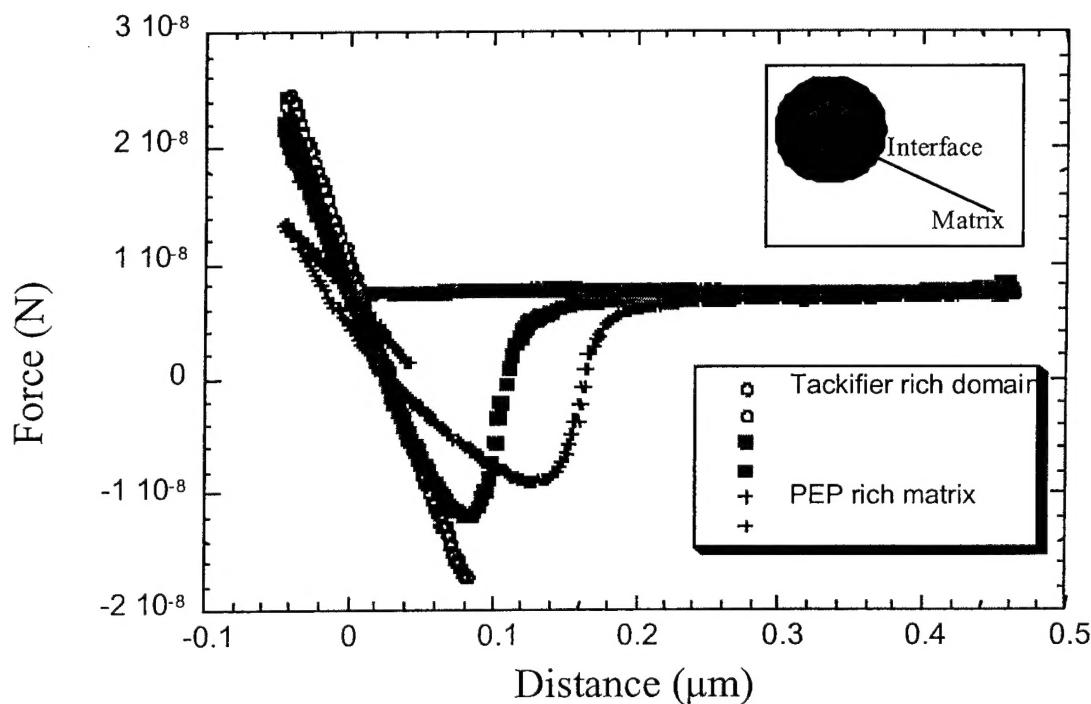
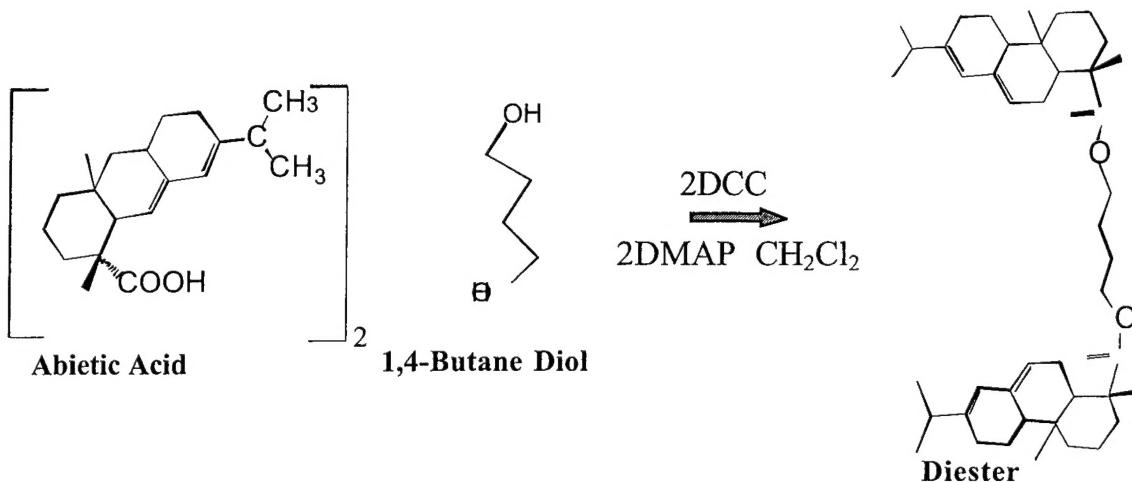


Figure 4. Force vs. distance curves for PEP/80 wt. % n-BEAA obtained using an AFM probe tip moving at $2.5\mu\text{m/s}$. Three behaviors are observed: viscoelastic response in domains, transition behavior close to the interface between phases and viscous behavior in the matrix. The inset shows schematically the line along which the measurements were taken.

Synthesis of a new tackifier

A new tackifier with larger molecular weight was synthesized in order to study the effect of molecular weight. The chemistry of the new tackifier, is, however analogous to that of the first one studied. It had not been anticipated that it would take so long to make the diester of abietic ester, shown below. Various practical difficulties in driving the reaction to a useful level of yield (ca. 70%), and successfully isolating the products from byproducts slowed the work. However, sufficient time remains to obtain some results on the changes in surface segregation with the variation in the tackifier.



ACKNOWLEDGEMENTS

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1999

In calendar year 1999 the doctoral student, Adriana Paiva-Ramirez, finished up her research, submitted two publications, wrote her thesis, and defended it successfully.

TECHNOLOGY TRANSFER

Just a few days before the award period actually began, as the final paper work was being completed, Prof. Foster made a trip to Dow Corning Corp. in Midland, Michigan, where he presented a talk entitled "Tackifier Surface Segregation in Pressure Sensitive Adhesives." Discussions with technical staff there dealt not only with tackifier migration's influence on adhesive performance, but also how the techniques developed in this work could be transferred to studies of additive migration and distribution in release coatings.

A poster presentation by Xiaoqing Li was given at the EPIC Semi-annual Review on October 12, 1995. This event brought together the academic and industrial members of a consortium supported in part by the state of Ohio. This consortium is intended to encourage technology transfer. Discussions ensued with technical personnel from B. F. Goodrich, TESA Tape, Inc., and ICI Glidden.

On August 14, 1996 Dr. Foster met with scientists from International Imaging Materials, Inc. who were visiting The University of Akron. Tackification of inks and surface migration were discussed in light of the results presented above. These results also have been shared with research personnel at TREMCO, a local manufacturer of sealants and adhesives.

Ken Chuang, a scientist at the Avery Dennison research center in Pasadena, California also discussed the work with Dr. Foster and Ms. Paiva after Ms. Paiva presented a talk on the material at the national meeting of the American Institute of Chemical Engineers in Chicago in November 1996. This discussion led to Dr. Foster's visiting the Avery Dennison research center in December, 1996.

Ms. Paiva-Ramirez was invited to take part in the Adhesion Gordon Conference in summer 1998 to present a poster on her work. Much of her expense to attend was underwritten by the Gordon Conference organization. She also presented her work in poster form at The University of Akron's Institute of Polymer Science Sponsors' Day technical session on Oct. 16, 1997 and at the Materials Network of Ohio Symposium at Bowling Green, Ohio on November 8, 1997.

Prof. Foster described the work briefly on March 7 in a meeting of the Ohio Consortium for Surface Engineering which was attended by representatives of several companies interested in the consortium including B. F. Goodrich, Libbey-Owens-Ford, Caterpillar, Dow Chemical, and Goodyear Tire and Rubber Co.

Ms. Paiva-Ramirez was invited to take part in the Science of Adhesion Gordon Conference in summer 1998 to present a poster on her work. Much of her expense to attend was underwritten by the Gordon Conference organization. She also presented her work in poster form at the Fall meeting of the Ohio Section of the American Physical Society. She received *third prize* for her poster.

In 1998 Presentations containing results from this project were presented at the Max-Planck-Institut für Polymerforschung (Nov. 18, 1998) in Mainz, Germany; The University of Freiburg in Freiburg, Germany; and at Research Center of Bridgestone/Firestone in Akron, Ohio.

Ms. Paiva-Ramirez presented her work at the Annual Meeting of The Adhesion Society in Panama City, FL. February '99. She was also invited to speak at the Pressure Sensitive Tape Council meeting in Washington, D.C. May '99. Her presentation at the American Institute of Chemical Engineers National Meeting in Dallas, TX. in November '99 received the *second place prize* in the student paper competition.

Two of the students trained under this grant have gone to firms with interests in adhesion. Xioaqing Li went to work for an adhesives firm (now owned by Ashland Chemical) after finishing her Ph.D. Adriana Paiva-Ramirez went to work for 3M.

Portions of the results presented here were discussed with the following individuals in the course of the project:

Prof. Kenneth Shull, Northwestern U.

Dr. David Speth, Dow Chemical

Dr. Cindy Chiu, Avery Dennison Research Center

Dr. Ken Chuang, Avery Dennison Research Center

Dr. Lilian Shum, Avery Dennison Research Center

Dr. Matt Muir, Goodyear Tire and Rubber Company

Privat Dozent Dr. Manfred Stamm, Max-Planck-Institut für Polymerforschung

Privat Dozent Dr. Jürgen Rühe, Max-Planck-Institut für Polymerforschung, Mainz, Germany

Privat Dozent Dr. Diethelm Johansmann, Max-Planck-Institut für Polymerforschung, Mainz

Privat Dozent Dr. Henning Menzel, U. Hannover

Dr. Hong Wu, Tesa Tape, Inc.

Dr. Donald Rimai, Eastman Kodak

Dr. Jim Baratucci, TREMCO, a local manufacturer of sealants and adhesives

The following individuals received a copy of one or more of the interim progress reports:

Dr. Cindy Chiu, Manager, Avery Dennison Research Center

Dr. Ken Chuang, Research Associate, Avery Dennison Research Center

Dr. Lilian Shum, Research Associate, Avery Dennison Research Center

Dr. Matt Muir, Goodyear Tire and Rubber Company

Dr. Jim Baratucci, Manager, Product Development,

TREMCO, a local manufacturer of sealants and adhesives

Dr. Hong Wu, Tesa Tape, Inc.

Dr. Gary Hagenauer, ARL

Dr. Nora Beck Tan, ARL

Dr. Wendel Shuely, Edgewood

Dr. Stephen S. Hupp, Corporate Research Director, Ashland Chemical

Dr. Stephen McKnight, ARL

Dr. Georg Böhm, Manager, Bridgestone/Firestone Research

Dr. Al Pocius, 3M Company

Dr. Xioaqing Li, Ashland Chemical - Central Adhesives

Dr. Marco Bommarito, 3M

Dr. David W. Dreifus, Director, Research and Development, Brady USA

Dr. Bernhard Momper, Clariant GmbH

Prof. J. Koberstein, U. Connecticut

Dr. Eric S. Gardiner, Arizona Chemical Company

Prof. Gary Hamed, U. Akron

Priv. Doz. Jürgen Rühe, Max-Planck-Institut für Polymerforschung